THE DETERMINATION OF ALKALI METALS, PARTICULARLY IN SILICATES.

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I N D E X.

THE DETERMINATION Of ALKALI METALS, PARTICULARLY In SILICATES.

The commoner alkali metals, sodium, potassium and lithium, exhibit a strong family resemblance in most properties, both chemical and physical. When it is considered that this resemblance includes their relative solubilities (with some notable exceptions), so that quantitative separation is rendered very difficult, it will be granted that there is ample scope for an investigation dealing solely with the determination of these metals.

In one branch of analytical work, the determination of the alkali metals is particularly important, namely, in the analysis of insoluble silicates, which are sometimes of extremely complex nature. The alkalies are, in practice, determined in a separate portion of the sample, the alkali chlorides being isolated from all other radicals. This has, up to the present, been the customary procedure, principally because soda has been determined by difference, and the total weight of alkali chlorides has been required.

Two methods of extracting the alkali chlorides are of outstanding importance. The older, that of Berzelius,[1)] consists of treating the powdered silicate

with a mixture of sulphuric and hydrofluoric acids. Subsequent evaporation, and treatment with ammonia separates silica, aluminium and iron; calcium and magnesium are precipitated in the extract. Sulphate is removed with barium chloride, the excess barium precipitated by repeated treatment with ammonium hydroxide and ammonium carbonate, and the ammonium salts expelled, leaving the mixed alkali chlorides. The method has several disadvantages, besides its complexity and the length of time required to complete it. The number of operations necessary to obtain the alkalies makes it almost inevitable that alkali contamination should be derived from the vessels and reagents used, while loss of alkali salts must take place, owing to adsorption during the precipitations, chiefly of lime and sulphate.

The second method, that of J. Lawrence Smith,[2] is extremely simple and effective, and is now regarded as one of the classic methods of modern analysis. It is a dry-way reaction between the finely powdered silicate, ammonium chloride and calcium carbonate, carried out in a covered platinum crucible at a temperature as high as is possible without causing volatilisation of the alkali chlorides formed. Subsequent extraction with water separates the alkali chlorides from a residue consisting mainly of calcium silicate and aluminate, and the carbonates of iron,

calcium and magnesium. The extract contains, in addition to the alkali chlorides, calcium hydroxide and a considerable amount of calcium chloride, with a trace of sulphate carried through from the silicate. The next step is the separation of calcium as carbonate, followed by the expulsion of ammonium salts and the removal of traces of contaminants, leaving a mixture of alkali chlorides as residue. There is a risk of loss by adsorption of alkalies in the calcium carbonate precipitation, and by volatilisation, if the temperature of expulsion of the ammonium salts is too high.

In view of the modern methods of determining sodium directly, by precipitation as complex triple acetates[3], the question arises, "How far is it necessary to proceed with the separation of other silicate constituents?" Caley and Foulk[4] used both of the foregoing methods of decomposing silicates, and determined sodium as sodium magnesium uranyl acetate, without prior removal of all other radicals, obtaining good results. As far as the time of decomposition is concerned, there is probably little to choose between the two methods, but that of Lawrence Smith is perhaps the more generally reliable for all types of silicates. Further, the aqueous extract obtained after decomposition of the silicate in this way is, as a rule, of simple composition, containing only the alkali chlorides, calcium chloride and hydroxide and a trace of sulphate. It was

accordingly proposed to investigate the determination of the commoner alkali metals, sodium, potassium and lithium, directly in the aqueous extract obtained after decomposing a silicate by the Lawrence Smith method, i.e. in presence of excess calcium salts and a little sulphate.

Sodium had previously been determined in presence of calcium chloride, both by the zinc uranyl acetate method of Barber and Kolthoff[5] and by the magnesium uranyl acetate method of Caley and Foulk[4]. These investigators found 0·825 gm. and 0·6 to 0·8 gm. respectively of hydrated calcium chloride to be without influence on the determination of about 0·01 gm. of sodium chloride. The zinc uranyl acetate method was selected for investigation because of its comparative simplicity and the definite composition of sodium zinc uranyl acetate. The magnesium uranyl acetate method, which involves a precipitate of variable water content, requires larger volumes of reagent and longer times of stirring, settling of the precipitate, etc., as compared with the other method. Guthrie and Miller,[6] working on the semi-micro-scale, determined sodium with the zinc uranyl acetate reagent in several silicates, in the extract from the silicate decomposition, without prior removal of calcium salts, and the results obtained did not show interference from the latter. Laboratory results of

silicate analyses on the large scale, however, showed some high results in cases where sodium was precipitated in presence of calcium salts, and the question of calcium contamination seemed to require investigation.

The customary procedure of separating the alkali chlorides from all other radicals has resulted in a dearth of information on the determination of potassium in presence of calcium salts. The perchlorate method and the sodium cobaltinitrite method have both, however, been successfully applied in presence of calcium salts, while the presence of an excess of calcium salts has been stated to have an accelerating effect on the reaction in the conductometric determination of potassium by precipitation as potassium calcium ferrocyanide.

In determining potassium as potassium perchlorate, Thin and Cumming[7] stated that all the perchlorates except those of potassium and ammonium were so soluble in the alcoholic solvent used that even 2 gm. of calcium chloride etc. could be present without affecting the results. Morris[8] also obtained good results with additions of calcium salts equivalent to 0·3 gm. of calcium chloride hexahydrate. With the introduction, however, of the ethyl acetate-n-butyl alcohol solvent by Smith and his co-workers,[9] little

or no data are available as to the influence of calcium salts on the determination; the investigators themselves deal only with "the mixed alkali chlorides, obtained by the Lawrence Smith or other method", and no mention whatever is made of other interfering radicals. Guthrie and Miller,[6] in their semi-micro-determinations, using ethyl acetate alone as solvent, found that it was advisable to remove calcium salts prior to converting to perchlorates.

The determination of potassium as potassium sodium cobaltinitrite[10] has been carried out in presence of calcium salts by Wassilieff and Matwejef,[11] who determined 0·5 gm. of potassium nitrate in presence of 1 gm. of hydrated calcium chloride, and by Piper[12] who determined 1 to 20 mg. of potash in presence of 0·66 gm. of calcium chloride. The former noted no interference, and the latter slight interference, particularly in determining the smaller amounts of potash.

The method has the great disadvantage that the composition of the precipitate depends to a large extent upon the conditions under which it is formed. Most investigators have been more concerned with studying this factor than the degree of completeness of precipitation.[13] Piper,[12] who dissolved up the precipitate and determined it volumetrically, claimed quantitative recovery of potassium, but even under the rigidly standardised conditions which he postulated, the

composition of the precipitate depended on the ratio of the sodium and potassium present, and a factor had to be applied in the calculation. Guthrie and Miller[6] discarded the method, since in their semi-micro-work they found that the presence of calcium chloride led to high results, and even when that was removed the results, using Hamid's method,[10] were very irregular. Hillebrand[14] recommended the treatment of the cobaltinitrite precipitate with perchloric acid and subsequent weighing of the potassium as the perchlorate. This procedure was thought to be of considerable value, provided the precipitation of potassium was quantitative.

No one appears to have examined the conductometric method of determining potassium in silicates by a simplified procedure, following decomposition by the Lawrence Smith method. Boulad[15] claimed an accuracy of ±1% in determining 0·015 gm. of potassium chloride in presence of calcium acetate equivalent to 0·02 to 0·04 gm. of hydrated calcium chloride.

The determination of lithium in silicates has invariably depended on the assembling of all the alkali chlorides, followed by the separation of lithium chloride and its conversion to lithium sulphate. Most investigators have been concerned with improving the separation process rather than with finding reagents for the determination of lithium. In their work on

sodium, Barber and Kolthoff[5] noted the sensitiveness of their zinc uranyl acetate reagent for sodium to lithium in solution and suggested the possible use of the reagent, saturated with the lithium triple acetate, for quantitative precipitation of lithium. With a reagent of this nature one would not, of course, expect to separate lithium from sodium,but other salts might not interfere. So far, no direct means of determining lithium in presence of calcium salts has been brought forward.

The following work is an account of investigations made to find the best means of determining soda, potash and lithia in silicates, without first of all separating completely the combined alkali chlorides. The methods developed for soda and potash refer in the first instance to silicates containing no lithia. Subsequent to the evolution of a method for the determination of lithia, suitable methods for the determination of all three constituents in the same silicate are indicated.

E X P E R I M E N T A L.

APPARATUS.

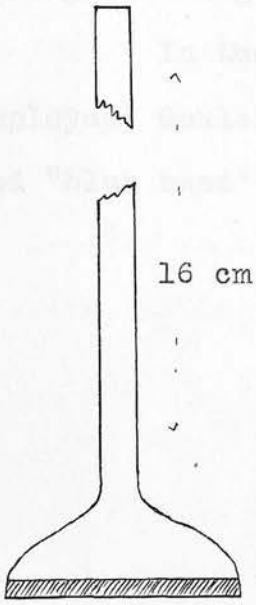


Fig. I - actual size.

All glassware used was either Pyrex or Jena. Jena sintered glass crucibles (No. 10 G4 and No. 10 G3) and quartz crucibles of 4-ml. capacity were used for filtering, filter-paper being avoided wherever possible. Specially designed small Jena glass immersion filters (G4) were very useful in some extraction processes (Fig. I).

Tall platinum crucibles (25 ml.) were used for the decomposition of silicates, and platinum basins of about 200 ml. capacity for the evaporation of the extracts. Small platinum basins (100 ml. and 60 ml.) were used in extraction processes and for weighing small residues.

Evaporations and heating were carried out on an electric hot-plate, or on a grid over an electric boiler. A low-temperature hot-plate was used for evaporating solvents of low boiling-point.

In the sodium and lithium triple acetate precipitations as many operations as possible were carried out in a gas-heated water bath, thermostatically regulated to approximately room temperature. All bottles of reagents required were kept clamped in the bath, and a wire rack was fitted to carry beakers during stirring etc.

In the few cases where filter-paper was employed, Schleicher and Schüll's No. 589 "white band" and "blue band" papers were used.

REAGENTS.

Acetone - from the bisulphite compound; shaken up with calcium carbonate (to remove any sulphur dioxide), refluxed over dried calcium chloride and fractionated. The fraction boiling at 55°C. at 730 mm. was used.

iso-Amyl alcohol - refluxed over metallic calcium and fractionated. The fraction boiling between 130°C. and 133°C. was used.

n-Butyl alcohol - fractionated. The fraction boiling between 112°C. and 118°C. was refluxed over metallic calcium for about four hours and fractionated. The fraction boiling between 116°C. and 117°C. was used.[9)]

Ethyl acetate - refluxed over phosphorus pentoxide for a day and fractionated. The fraction boiling between 76·5°C. and 77·5°C. was used.[9)]

Ethyl alcohol and ether were redistilled. The ether was anhydrous.

Ammonium chloride - Kahlbaum's "for analysis".

Ammonium hydroxide - A.R., distilled from a Pyrex apparatus on a water bath. It was passed into a 2-litre waxed Jena glass bottle, about one-third filled with distilled water and cooled in a mixture of ice and water. The distillation was stopped when the density of the ammonium hydroxide reached 0·95 gm. per ml., corresponding to a normality of approximately 6·5.

Calcium carbonate - A.R. A specially washed sample was prepared for this work by Hopkin and Williams.

Calcium chloride, $CaCl_2.6H_2O$ - Kahlbaum's "mit garantieschein". It was examined spectroscopically by Dr S. Judd Lewis and guaranteed to contain not more than 0·0002% of sodium, and probably 10% to 15% less.

Hydrochloric acid - A.R., redistilled from an all-Pyrex apparatus (distillate 6·7 N), and kept in a Jena glass bottle.

Lithium carbonate - Merck's "extra pure". It was examined spectroscopically by Dr S. Judd Lewis and guaranteed to contain not more than 0·014% of sodium. A sample lost no weight on heating to 200°C.

Perchloric acid - A.R., purified by heating to 200° at atmospheric pressure, and then distilling under a few mm. pressure in an all-Pyrex apparatus, using a calcium chloride bath at 130°C. to 140°C.[16] The perchloric acid so obtained was of about 70% strength (S.G. 1·68), and left no weighable residue on evaporation.

Potassium chloride - Kahlbaum's, recrystallised from conductivity water, dried and heated to fusion with a Méker burner.

Sodium chloride - Kahlbaum's "mit garantieschein", dried and heated to fusion with a Méker burner.

All other reagents were of A.R. quality.

SODIUM.

The Sodium Content of the Calcium Carbonate used for the Decomposition of Silicates by the Lawrence Smith Method.

In the decomposition of a silicate by the Lawrence Smith method, the purity of the reagents used is all-important, as any alkalies present will pass into the extract, causing high results. The large weight of calcium carbonate used (4 gm.) makes this reagent especially important and, in order to arrive at true values for the alkalies in the silicate, knowledge of the exact amount of alkali contamination in the calcium carbonate (almost exclusively sodium salts, c.f. Hillebrand and Lundell, "Applied Inorganic Analysis", 1929, p. 788) is absolutely essential.

It is generally recognised that mere extraction of the calcium carbonate with water will not enable one to remove and determine the whole of the alkali salts present as impurity.[17) 18)] In the determination of soda in silicates it is therefore customary to carry out an experiment with the reagents alone, in order to find the amount of sodium derived from them. In careful work the source of practically all the sodium impurity is the calcium carbonate. Thus there might be a saving of time in selecting a suitable sample of calcium carbonate if a more direct determination could be made of the sodium content.

Caley[19] determined the sodium contamination in 2 gm. of calcium carbonate by dissolving the sample in hydrochloric acid, evaporating and precipitating the sodium as sodium magnesium uranyl acetate. In this way he obtained much higher figures than those given by water extraction processes. Kolthoff and Sandell[20] also determined directly, by the zinc uranyl acetate method, the amount of sodium contamination in calcium oxalate precipitates previously converted to calcium carbonate. In both cases, however, it was found necessary to leave the mixtures overnight to ensure maximum deposition of the small amount of sodium triple acetate, and there is no means of assessing the accuracy of the results.

It was proposed to examine more closely the direct method of determining sodium in calcium carbonate by means of the zinc uranyl acetate reagent, and to compare the results with those obtained after treating the calcium carbonate as in the decomposition of a silicate.

As a preliminary to this a few determinations of sodium were made, first in pure sodium chloride solutions and then in presence of practically sodium-free calcium chloride.

The Precipitation of Sodium as Sodium Zinc Uranyl Acetate in Absence of Calcium Chloride.

A solution of zinc and uranyl acetates, saturated with sodium zinc uranyl acetate, was prepared

according to Barber and Kolthoff's[5] recommendations, and kept in a thermostat near room temperature. Two sodium chloride solutions were used, one containing 0·01 gm. of sodium chloride per ml. and the other 0·001 gm. of sodium chloride per ml., both being made up by weight and appropriate volumes weighed out for analysis in 50 ml. beakers.

To the sodium chloride solution 10 ml. of the filtered reagent were added and the mixture was stirred. It was set aside for 30 minutes in the thermostat, filtered through a sintered glass crucible (No. 10 G3), and the precipitate was washed with five 2-ml. portions of filtered reagent, five 2-ml. portions of a filtered wash-solution, consisting of 95% ethyl alcohol saturated with the triple salt at the thermostat temperature, and finally with three 2-ml. portions of redistilled ether. It was important not to wash the precipitate too rapidly with the alcoholic wash-liquid, in order to ensure complete removal of the precipitant. The precipitate was dried at 40°C. for ten minutes, cooled for ten minutes and weighed.

TABLE I.

NaCl Used (gm. × 10^5)	NaCl Found. (gm. × 10^5)	Error (gm. × 10^5)
1000	1000	0
	995*	-5
500	501	+1
	498	-2
200	197	-3
	191*	-9
100	97	-3
	98	-2
50	50	0
	48	-2

* The crucible used in these experiments was subsequently rejected as giving consistently low results.

The Precipitation of Sodium as Sodium Zinc Uranyl Acetate in Presence of Calcium Chloride.

To 0·001 gm. of sodium chloride in 1 ml. of water, 12 gm. of calcium chloride ($CaCl_2.6H_2O$ ≡ 5 gm. of calcium carbonate) were added, with about $1\frac{1}{2}$ ml. of water to bring the volume to 10 ml. As the reagent

must be present in ten-fold excess, 100 ml. of the filtered reagent were added. To ensure the maximum deposition of the sodium triple acetate, the mixture was mechanically stirred for 30 minutes and left for 15 minutes before filtering and washing as usual. In spite of these precautions only 75% recovery was obtained.

This means that a very small amount of sodium chloride, present in the calcium carbonate, cannot be accurately and rapidly determined directly. The next step was to find whether theoretical results could be obtained by addition of the calcium chloride solution to a larger amount of sodium chloride. The previous experiment was therefore repeated, using 0·01 gm. of sodium chloride, the sodium triple acetate being precipitated and stirred as before. At the same time a similar experiment was carried out in absence of calcium chloride, with 0·01 gm. of sodium chloride diluted to 10 ml., and addition of 100 ml. of the precipitating reagent.

In absence of calcium chloride the result was 0·5% low, and in its presence 7·4% high. The latter suggests contamination of the triple salt by calcium salts, but probably almost complete precipitation. The fact that Barber and Kolthoff[5] found only a small positive error (+0·5%) in determining 14·6 mg. of sodium chloride in 1 ml. of a solution containing 0·825 gm. of calcium chloride may be explained by compensating errors

due to contamination of the precipitate and to incomplete precipitation.

From the above results it would seem desirable in determining a small amount of sodium in calcium carbonate to augment it by adding a known amount of sodium chloride of the order of 10 mg. A means of freeing the impure precipitate from its contaminants was now sought.

The Double Precipitation of Sodium Zinc Uranyl Acetate in Absence and in Presence of Calcium Salts.

The most obvious means of removing contaminants from sodium zinc uranyl acetate seemed to be reprecipitation. The process was first carried out qualitatively with precipitates prepared from pure sodium chloride. It was found that, when 10 ml. of 0·1 N acetic acid were used to dissolve the precipitate from 0·01 gm. of sodium chloride, solid separated out from the solution on evaporation, before a volume of 2 ml. was reached. On addition of 1 ml. of N hydrochloric acid it redissolved and remained in solution on evaporation to 2 ml. It was therefore better to dissolve the precipitate in 10 ml. of 0·1 N hydrochloric acid and evaporate to 2 ml.

Experiments were now made quantitatively with 0·01 gm. of sodium chloride. The first precipitation was made from 10 ml. of solution, with 100 ml. of the

precipitating reagent, with the same stirring etc. as given to the calcium-containing solutions. The first precipitate was separated, washed, dried and weighed as usual, and dissolved in 10 ml. of 0·1 N hydrochloric acid. The solution was collected in a crucible placed within the Gooch adapter, transferred to a 50 ml. beaker, evaporated to 2 ml. and treated with 20 ml. of the precipitant. 15 minutes' stirring and 15 minutes' settling followed, and the filtering and washing of the precipitate were carried out as before.

Double precipitations were carried through, in exactly the same manner, of 0·01 gm. of sodium chloride from 10 ml. of solution containing varying amounts of calcium chloride, as shown in Table II. The results are corrected for the small amount of sodium present in the calcium chloride (p. 12).

TABLE II.

Wt. NaCl used = 0·01000 gm.

$CaCl_2 \cdot 6H_2O$ Used (gm.)	NaCl Found (one pptn.) (gm. x 10^5)	NaCl Found (two ppts.) (gm. x 10^5)	Error after one ppt. (gm. x 10^5)	Error after two ppts. (gm. x 10^5)	Loss in wt. on second ppt. (gm. x 10^5)
0·0	995	971	-5	-29	24
	986	973	-14	-27	13
	998	992	-2	-8	6
0·5	1007	981	+7	-19	26
	1005	979	+5	-21	26
1·0	1016	991	+16	-9	25
	1016	993	+16	-7	23
3·0	1055	996	+55	-4	59
5·0	1079	994	+79	-6	85
	1060	980	+60	-20	80
12·0	1074	989	+74	-11	85
	1081	967	+81	-33	114

These figures show quite definitely that, with increasing calcium content of the original solution, there is an increasing amount of contamination of the first precipitate, and that the calcium chloride is not interfering with the degree of completeness of the precipitation of 10 mg. of sodium chloride. The irregularity in the figures of the second last column is probably covered by experimental error, and it is evident that an average correction of +0·16 mg. of sodium chloride will have to be applied when about 10 mg. of sodium chloride are determined after a double precipitation in presence of amounts of hydrated calcium chloride up to 12 gm.

The Determination of Sodium in Calcium Carbonate.

Hopkin and Williams's "specially washed" calcium carbonate, which it was proposed to use for decomposing the silicates, was tested in the following way. 5 gm. of the calcium carbonate in a platinum basin were dissolved in 20 ml. of 6·7 N hydrochloric acid and carefully evaporated to dryness on the electric boiler; water was added to make 7 to 8 ml. The solution was then washed out into a 250 ml. beaker containing 0·01 gm. of sodium chloride, with 100 ml. of the precipitating reagent, and sodium was determined as prescribed on p.18.

Simultaneously, 4 gm. of the same calcium carbonate were heated with 0·5 gm. of pure ammonium chloride according to the Lawrence Smith method for decomposing silicates (p. 28). The extract, acidified

with 1 ml. of 6·7 N hydrochloric acid, was evaporated to dryness on the electric boiler and the residue was added to 0·01 gm. of sodium chloride. The triple salt was precipitated from 10 ml. of solution with 100 ml. of reagent, dissolved up and reprecipitated as previously.

The results for both sets of determinations are shown below. In the third column the correction referred to on p. 20, viz. +0·16 mg. of sodium chloride, has been applied.

TABLE III.

NaCl added = 0·01000 gm.

$CaCO_3$ Used	NaCl Found (two pptns.) (gm. × 10^5)	NaCl in $CaCO_3$ Used (gm. × 10^5)	Average NaCl in 4 gm. $CaCO_3$ (gm. × 10^5)
Direct Determination:			
5 gm.	1043	59	47
	1043	59	
Determination in Extract after heating with NH_4Cl:			
4 gm.	1036	52	49
	1029	45	

The above results show that, provided the other reagents are pure, the direct determination of the sodium content of calcium carbonate may satisfactorily replace its determination subsequent to heating the carbonate with ammonium chloride, etc., as in the

decomposition of a silicate.

Precipitated Calcium Oxalate as a Source of Pure Calcium Carbonate.

As Kolthoff and Sandell[20] have shown that calcium oxalate can be precipitated from calcium chloride solution in a very pure state under certain conditions, an attempt was made to prepare a purer sample of calcium carbonate by heating calcium oxalate formed under these conditions.

50 gm. of pure calcite in a platinum basin were dissolved in 200 ml. of 6·7 N hydrochloric acid, diluted with distilled water in a beaker to about two litres, and 63 gm. of oxalic acid, dissolved in slightly over one litre of distilled water, were added. The solution was then neutralised with 6·5 N ammonium hydroxide, and kept near the boiling-point for 24 hours to promote the formation of a more granular precipitate. The supernatant liquid was removed by means of a sintered Jena glass immersion filter (No. 36 G3) and washed with about a litre of water in 100 ml. portions. The precipitate was then transferred to a large sintered Jena glass filter (No. 25 G3), washed again and dried in a platinum basin at 105° in an electric oven for one day.

A trial experiment was made to find if calcium oxalate could itself be used in the decomposition of a silicate (p. 28). It was found, however,

that great care was essential during the decomposition, especially in the early stages, since ignition of the carbon monoxide evolved in the decomposition of the oxalate was liable to occur, with danger of low results.

Conversion of the calcium oxalate to calcium carbonate was effected by heating in an electric furnace at 450°C. to 500°C.[21] Slight charring indicated that carbon would have to be filtered off prior to the determination of the sodium content of the calcium carbonate. When this was omitted, the carbon tended to prevent settling of the sodium triple acetate.

The direct determination of sodium in the calcium carbonate so prepared, with addition of 0·01 gm. of sodium chloride as usual, showed that 4 gm. contained 0·26 mg. of sodium chloride (average of three determinations).

It was feared, however, that the carbon in the calcium carbonate might lead to low results by producing a reducing atmosphere during the silicate decomposition; its use, therefore, was not further considered and the "specially washed" calcium carbonate was employed in all later experiments.

<u>The Determination of Sodium under the Conditions prevailing in Silicate Analyses</u>.

As mentioned in the introductory section, the aqueous extract obtained after decomposing a silicate by the Lawrence Smith method usually contains, in

addition to the chlorides of the alkali metals, calcium chloride and hydroxide, with a trace of sulphate. Two silicates of different type, namely, "Plastic Clay, No. 98" and "Opal Glass, No. 91" from the American Bureau of Standards, were decomposed in order to determine approximately the amounts of calcium salts present in the filtrate from the extraction process. 0·004 gm. of ammonium sulphate was added to increase the sulphur content of the clay. In both aqueous extracts calcium was precipitated as oxalate, the precipitate was dissolved up in acid and titrated with a standard potassium permanganate solution. The amount of calcium was found to be equivalent to 1·2 gm. of hydrated calcium chloride (or 0·55 gm. of calcium carbonate). In the extract from the decomposition of the clay 0·0043 gm. of barium sulphate was precipitated.

In the silicate analyses, since not more than 8 mg. of sodium per ml. of solution can be determined by the zinc uranyl acetate method, and the percentage of sodium in the triple acetate is small, it was proposed to determine sodium only in a small portion of the acidified silicate extract - one-tenth or one-fifth, according to the sodium content - reserving the remainder for the determination of potassium (p. 32). This meant that the amount of calcium chloride present would be correspondingly reduced to 0·12 gm. or 0·24 gm. of the hexahydrate. Experiments were therefore carried out to

see if a double precipitation of sodium zinc uranyl acetate would be necessary in presence of these amounts of calcium chloride. From Table II it might be predicted that, if the initial volume of solution from which sodium was precipitated was 1 ml., the amount of contamination in presence of 0·12 gm. of calcium chloride would be approximately 0·16 mg., i.e. of the order of that obtained in presence of 1 gm. of calcium chloride, where the initial volume of the solution was 10 ml.

Experiments were now carried out with mixtures containing amounts of sodium and calcium chlorides that would be equivalent to those present in one-tenth or one-fifth of the extract derived after decomposing half a gram of silicate containing approximately 10%, 5%, 0·5% and 0·25% of soda.

The sodium chloride and calcium chloride solutions, along with 1 ml. of 0·1 N hydrochloric acid (to make the conditions comparable with those of the silicate extract) were evaporated on the steam-bath to not more than 1 ml. volume and the sodium was precipitated with 10 ml. of the zinc uranyl acetate reagent. Thirty minutes' stirring and 15 minutes' settling of the precipitate followed, and the precipitate was separated and weighed. It was then dissolved in 10 ml. of 0·1 N hydrochloric acid (5 ml. for the smaller amounts) evaporated to 2 ml. and reprecipitated with

20 ml. of the reagent; stirring was effected for 15 minutes and the precipitate was allowed to settle for 15 minutes, separated and weighed. The results are shown in the upper section of Table IV which is self-explanatory.

All the results of the first precipitations in presence of calcium chloride were high, but it was found that in some cases the figures showed as large or larger errors in the opposite direction after two precipitations. This, it was thought, might be due to loss of the precipitate through the filtering crucibles (No. 10G3), especially as the precipitate in presence of calcium was very finely divided. No. 10 G4 crucibles were substituted, but were found to be too slow-filtering. A very thin layer of asbestos was then introduced into the No. 10 G3 crucibles, with satisfactory results. Since it was evident that a double precipitation was necessary, experiments were afterwards carried through in a simplified manner. The first precipitate was transferred to the crucible, washed with reagent as usual and then with two 1-ml. portions of the alcoholic wash-liquid. The solution of the precipitate and the reprecipitation were effected as before. Improved results, embodying these modifications are shown in the lower section of Table IV.

TABLE IV.

Wt. $CaCl_2.6H_2O$ (gm.)	NaCl Used (gm. × 10^5)	NaCl Found (one pptn.) (gm. × 10^5)	NaCl Found (two pptns.) (gm. × 10^5)	Error after one pptn. (gm. × 10^5)	Error after two pptns. (gm. × 10^5)	Loss on second pptn. (gm. × 10^5)
0.12	1000	1010	1003	+10	+3	7
		1012	994	+12	-6	18
0.12	500	514	504	+14	+4	10
		512	494	+12	-6	18
0.24	100	104	95	+4	-5	9
		106	99	+6	-1	7
0.24	50	56	42	+6	-8	14
		56	45	+6	-5	11
0.12	1000		998		-2	
			997		-3	
0.24	50		48		-2	
			50		0	

The Direct Determination of Soda in Silicates.

Experiments were now made to show the application of the above method to the determination of soda in the following silicates - 'Plastic Clay, No. 98', 'Opal Glass, No. 91', 'Feldspar, No. 70' and 'Burnt Refractory, No. 76' - all of which had certificates of analysis from the American Bureau of Standards.

The details of procedure were those given by Washington (The Chemical Analysis of Rocks, 1930, p.222).

The powdered silicate was dried before use at the temperature quoted in the certificate. 0·5 gm. was weighed by difference into a large agate mortar, and mixed thoroughly with 0·5 gm. of ammonium chloride by means of an agate pestle. 4 gm. of calcium carbonate were weighed out, and about two-thirds were added in small portions to the mixture in the mortar, with thorough mixing each time. A little calcium carbonate was placed in the bottom of a platinum crucible, standing on a sheet of glazed paper, and the mixture in the mortar was carefully transferred to it by means of a spatula, the mortar and pestle being rinsed by grinding round the rest of the calcium carbonate in small portions and adding them to the contents of the crucible.

The crucible was covered with a tightly fitting lid and inserted in a hole, cut in a slightly inclined asbestos board, just sufficiently large to admit the lower third. The crucible was heated, gently

at first, until all ammonium salts ceased to be evolved, and then strongly (until the bottom of the crucible was bright red) for 40 minutes. After cooling, the contents were slaked with a little water and the crucible was set aside for a few minutes, when the sintered cake should have become quite soft and easy to remove. It was transferred by a jet of hot water to a platinum basin (about 100 ml. capacity and preferably of thick platinum), the final volume not exceeding 50 ml. The mass was ground up with an agate pestle, the pestle rinsed, and the mixture heated to boiling for a few minutes. The liquid was then decanted through a 7-cm. "white-band" filter-paper into a 400 ml. beaker, and a little more water was added to the residue, which was broken up again and boiled. The liquid was again decanted, more water was added to the residue, and finally, after boiling the mixture, the whole residue was brought on the filter and washed thoroughly with hot water in small portions, until the total volume of filtrate reached 200 ml. The extract was acidified with 1 ml. of concentrated hydrochloric acid and made up to 250 ml. in a standard flask. For sodium determinations, 25 ml. were used in the case of the 'Opal Glass' and the 'Feldspar' and 50 ml. in the case of the 'Plastic Clay' and the 'Burnt Refractory'. Each figure given below represents a separate decomposition of the silicate, and a correction of -0·05% has been applied for sodium in the reagents (p. 21). The table

shows, in addition, the Bureau of Standards figures, and the maximum deviation from the mean, in percentages of the whole rock, allowed by Washington (The Chemical Analysis of Rocks, 1930, p. 142).

TABLE V.

Silicate Used.	Percentage of Soda.		Mean Percentage, Experimental.	Maximum Deviation from Mean.	Maximum Deviation allowed by Washington.
	Bureau of Standards Figure.	Experimental			
OPAL GLASS	8·46	8·39 8·50 8·32	8·40	+0·1 -0·08	±0·05
FELDSPAR	2·38	2·35 2·33	2·34	±0·01	±0·05
BURNT REFRAC-TORY	0·38	0·19 0·17 0·20* 0·20*	0·18 0·20	±0·01 ±0	±0·03
PLASTIC CLAY	0·27	0·25 0·25	0·25	±0	±0·03

* further ground.

From the above table it is seen that all the separate determinations, with the exception of those for the 'Opal Glass', which was known to be rather difficult to decompose, agree well with each other, the variations being within the limits allowed by Washington. The only figure not in good agreement with the certificate is that for the 'Burnt Refractory'. Because of this,

two determinations were made after further grinding of the sample so as to be absolutely sure of complete decomposition, but only slightly higher figures were obtained. There is no reason to suppose that the figures given are seriously in error. It is significant that the results for potash subsequently found (p. 51) are high by amounts roughly equivalent to the amounts by which the results for soda are low, as referred to the certificate values.

POTASSIUM.

After the decomposition of a silicate by the Lawrence Smith method and extraction with water, it was proposed to determine potassium in as direct a manner as possible in the major portion of the solution remaining after removal of part for the determination of sodium (p. 24). The main problem was, therefore, to find the best means of determining potassium in presence of a large excess of calcium salts and a little sulphate. As mentioned in the introduction, there is very little information available on the determination of potassium in presence of calcium salts.

Following the procedure in the case of sodium, experiments with synthetic mixtures, similar in composition to the solutions obtained in silicate analyses, preceded the actual determination of potash in silicates.

The method of determining potassium by conductometric titration with calcium ferrocyanide [15] received brief consideration, mainly on account of its applicability in presence of calcium salts. The proportion of calcium to potassium, under the conditions postulated here, was however very much greater than in Boulad's work (p. 7), with the consequence that conductivity changes during titration were much less. A number of experiments were carried out in which all precautions were taken to reduce to a minimum the errors

associated with the actual conductivity measurements, but even so, no results of any practical value were obtained and they are not recorded.

The following description of experimental work is entirely concerned with the final weighing of potassium as perchlorate.

Method (a). The Determination of Potassium as Potassium Perchlorate in Presence of Calcium Salts.

In the extract obtained after decomposing a silicate by the Lawrence Smith method, there may be 0·1 gm. each of sodium and potassium chlorides present, with 1·2 gm. of hydrated calcium chloride and a little sulphate (p. 23). As calcium perchlorate is very soluble in organic solvents in which sodium perchlorate is soluble, Guthrie and Miller,[6] in their semi-micro-work, sought to separate potassium from sodium and calcium by converting the chlorides to perchlorates and extracting with ethyl acetate in which the solubility of potassium perchlorate is very small. They stated, however, that complete removal of the calcium contamination was only possible after repeated extractions with the solvent, and they preferred to precipitate the calcium as calcium carbonate, and to expel ammonium salts, prior to the conversion to the perchlorates. On the large scale, however, it was thought that removal of the calcium perchlorate might

be effected without appreciable loss of potassium perchlorate and without the necessity for an excessive number of extractions, by using as solvent the ethyl acetate - n-butyl alcohol mixture of Smith and his co-workers[9] in which calcium perchlorate is likely to be more soluble than in ethyl acetate itself (Hillebrand and Lundell, p. 253).

Preliminary experiments were carried out with potassium chloride alone, using amounts of a potassium chloride solution containing from 0·1 to 0·005 gm. of potassium chloride. To the solution was added two to three times the equivalent quantity of perchloric acid (not less than 1 ml. of 60% to 70% acid), and the mixture was evaporated to dryness in a small weighed platinum basin. The residue was dissolved in the minimum amount of hot water and the solution was again evaporated to dryness. 10 ml. of a mixture of equal parts by volume of ethyl acetate and n-butyl alcohol were added, and the mixture was digested near the boiling point for two or three minutes. The residue was broken up with a flat-ended stirring rod, and the solution was cooled to room temperature and decanted through a Jena glass filtering crucible (No. 10 G 4). The residue was washed five times by decantation with 2-ml. portions of the solvent and dissolved in the minimum amount of hot water, the small amount of residue in the crucible being washed out and added to the solution, which

was again evaporated to dryness. The residue was once more extracted with 10 ml. of the solvent, digested, cooled and filtered. The potassium perchlorate was transferred to the crucible and washed with five 2-ml. portions of solvent. It was then dissolved out into a filter-tube and the solution added to any residue left in the platinum basin. The contents of the basin were evaporated to dryness on the steam-bath, heated for a few minutes at 150°, to prevent decrepitation, and finally heated for 10 minutes at 350° in the electric furnace, cooled and weighed.

A considerable saving of time was effected, and the manipulation was rendered much more simple, by the substitution of a specially small sintered Jena glass immersion filter (p. 9) for the crucible in the extractions. It was connected by pressure tubing (through a 500 ml. filter flask to act as a trap) to the filter-pump, and inserted in the mixture to be extracted. Suction was applied to remove the liquid, and the basin and contents were rinsed with five 1-ml. portions of the solvent, each portion being carefully removed before addition of the next. If necessary, the filter was carefully raised and inverted to allow the liquid within it to drain back into the flask. The filter was then disconnected and rinsed thoroughly externally with boiling water. Three 2-ml. portions of boiling water were passed down inside the filter and

forced through by connecting to the air-blast, or simply by blowing through, and the exterior was once more rinsed. The water used was generally sufficient to dissolve the residue which was evaporated down in the same basin for repetition of the extraction process. Finally the residual potassium perchlorate was weighed as before in the basin. The results, which were satisfactory, are shown in Table VI.

TABLE VI.

KCl Used (gm. × 10^4)	KCl Found (gm. × 10^4)	Error (gm. × 10^4)
1000	1001	+1
	999	-1
	1004 *	+4
	1002 *	+2
500	498	-2
200	199	-1
50	51	+1

* Immersion filter used.

Experiments were next made on the determination of potassium in the presence of calcium and sodium chlorides.

1·2 gm. of calcium chloride hexahydrate were added to the potassium chloride solution to be determined. As before, the chlorides were converted to perchlorates, but the conversion was troublesome, due, in

part, to the retention of the perchloric acid by the mixed perchlorates. Even with comparatively strong heating over the electric boiler, a process which, incidentally, did not affect the final results, the removal of the last traces of perchloric acid was difficult. Two extractions of the mixed perchlorates were made. The first calcium-rich extract was extremely slow-filtering.

In spite of these defects, the results obtained for potassium were quite good, and additions of 1·2 gm. of calcium chloride and 0·1 gm. of sodium chloride to the potassium chloride solution were now made.

The figures shown in the table below indicate that satisfactory results were obtained for potassium when only two extractions were made with the requisite solvent (p. 34).

TABLE VII.

KCl Used. (gm. x 10^4)	KCl Found. (gm. x 10^4)	Error. (gm. x 10^4)	$CaCl_2 \cdot 6H_2O$ added (gm.)	NaCl added (gm.)
1000	995	-5	1·2	0
	1001	+1	"	"
	1002 *	+2	"	"
50	52 *	+2	"	"
1000	1003	+3	1·2	0·1
	1002	+2	"	"
	997	-3	"	"

* Immersion filter used.

Finally the sulphate radical was introduced. Since sodium sulphate cannot be converted to perchlorate by evaporation with perchloric acid[8], and moreover is insoluble in the alcoholic solvent, it is necessary to remove the sulphate ion by precipitation with barium chloride, excess of which, if converted to barium perchlorate, may be extracted along with the calcium and sodium perchlorates. A small amount of soluble sulphate (0·005 gm. of sodium sulphate) was accordingly added to mixtures containing sodium and calcium chlorides as above, and amounts of potassium chloride corresponding to approximately 12%, 6% and 0·6% of potash in half a gram of silicate.

The solution was diluted to 100 ml. in a platinum basin and 2 ml. of a 1% aqueous barium chloride solution were added to precipitate the sulphate. The solution was evaporated to 10 ml. and filtered through a very small "blue-band" ashless filter-paper, directly into the weighed platinum basin. To diminish solubility errors, it was advisable to filter cold and to wash with cold water. Owing to the solubility of barium sulphate in solutions containing hydrochloric acid[8] it was essential to precipitate barium sulphate in neutral solution. This meant that, in silicate determinations, the acidified extract would have to be evaporated to dryness to remove excess acid and redissolved in water prior to the precipitation of the

barium sulphate.

The filtrate from the barium sulphate was evaporated down with perchloric acid and extracted twice with the ethyl acetate - n-butyl alcohol mixture, and the residual potassium perchlorate weighed. An important point here was the necessity for electrical heating in all cases where heat was required subsequent to the filtration of the barium sulphate. This precluded any possibility of the formation of more barium sulphate by interaction of the excess barium ions and sulphate from sulphur in the coal-gas.

The results obtained, which are quite satisfactory, are shown in Table VIII below.

TABLE VIII.

KCl Used (gm. × 10^4)	KCl Found (gm. × 10^4)	Error (gm. × 10^4)
1000	1002	+2
	1002	+2
500	502	+2
50	54	+4
	48	-2
	53	+3

A few determinations of potash in silicates were now made.

The Determination of Potash in Silicates by Method (a).

Potash was determined in the silicates 'Feldspar, No. 70', 'Plastic Clay, No. 98' and 'Burnt Refractory, No. 76' of the American Bureau of Standards, 0·5 gm. of each silicate being decomposed according to the method of Lawrence Smith (p. 28). The total extract in each case was acidified with 1 ml. of 6·7 N hydrochloric acid, made up to 250 ml., and as much as possible (depending on the volume that would be used for the soda determination) was used for the potash determination. The portion used was evaporated to dryness, the residue dissolved in water and barium sulphate precipitated. The conversion to perchlorates and extractions with the ethyl acetate - n-butyl alcohol mixture were exactly as described above. The results are given below, along with the American Bureau of Standards figures.

TABLE IX.

Silicate Used	Percentage of Potash	
	Bureau of Standards	Experimental
FELDSPAR	12·58	12·56
PLASTIC CLAY	3·20	3·12, 3·30 } 3·21
BURNT REFRACTORY	1·37	1·60, 1·65 } 1·63

The only result which is widely divergent from that of the Bureau of Standards certificate is that for the 'Burnt Refractory'. The agreement in the duplicate results for the 'Plastic Clay' is fair.

Although the high figures for the 'Burnt Refractory' were borne out by later experiments made by slightly different methods, they were at this stage thought to be associated with experimental errors. As Karaoglanov[22] has shown that barium sulphate is very slightly soluble in calcium chloride solutions, particularly those containing potassium and sodium chlorides as well, the method of precipitating barium sulphate was regarded as a potential source of error. The following experiments were made. Solutions containing sodium and calcium chlorides and a little sulphate, in the usual proportions, but no potassium chloride, were submitted to the customary treatment for the separation of potassium as potassium perchlorate. Small residues, weighing 0·4 mg. to 1·1 mg., were ultimately obtained, and, after suitable treatment, found, by testing with a sodium rhodizonate solution, to contain barium ions. The above amounts of barium sulphate weighed with potassium perchlorate would not, however, account entirely for the positive errors noted in the determination of potash in the 'Burnt Refractory'.

As stated on p. 36, the method outlined for the determination of potassium had several disadvantages in addition to that cited above. In view of these, it

was considered advisable to remove calcium salts, at least qualitatively, prior to the separation of barium sulphate, and the conversion of potassium chloride etc. to the perchlorates. In this connection it was proposed to use an alcohol for the removal of calcium chloride, as described in the following section.

Method (b). The Determination of Potassium as Potassium Perchlorate after the Preliminary Removal of Calcium Chloride by means of an Alcohol.

In using an alcohol to extract calcium chloride from the mixed chlorides, the important points were to dehydrate the chlorides adequately and to avoid partial solution of the potassium chloride in the alcohol selected. Preliminary experiments were made with (a) absolute ethyl alcohol, (b) n-butyl alcohol, and (c) iso-amyl alcohol as solvents.

The solution containing the chlorides of potassium (0·1 gm. to 0·005 gm.), sodium (0·1 gm.), and calcium (1·2 gm.), and sodium sulphate (0·005 gm.) was evaporated to dryness and extracted with 10 ml. of the alcohol, the immersion filter (p. 9) being used to remove as much as possible of the solution. The residue was dissolved in hot water, the alcohol very carefully evaporated, 10 ml. of water were added, and the barium sulphate was precipitated. To obviate adsorption

errors that might be introduced by the use of filter-paper, the solution was filtered, cold, through a tiny quartz, asbestos-lined, crucible directly into a weighed platinum basin, placed within a Gibson filtration apparatus (Hillebrand and Lundell, p. 92). The treatment with perchloric acid followed by two extractions was carried out as usual.

All three solvents gave satisfactory results, as shown by Table X, but in subsequent work it was thought safer to use the iso-amyl alcohol, in which the solubility of potassium chloride is least.

TABLE X.

Solvent	KCl Used (gm. × 10^4)	KCl Found (gm. × 10^4)	Error (gm. × 10^4)
Ethyl Alcohol	1000	1000	0
	50	49	-1
n-Butyl Alcohol	100	98	-2
	50	50	0
	50	49	-1
Iso-Amyl Alcohol	1000	1000	0
	50	47	-3
	50	52	+2

The Determination of Potash in Silicates by Method (b)

Potash was determined in the silicates 'Feldspar, No. 70', 'Plastic Clay, No. 98' and 'Burnt

Refractory, No. 76' of the Bureau of Standards, and 'Inchcolm Picrite' analysed by T. C. Day.[23] 0·5 gm. of the silicate was decomposed according to the method of Lawrence Smith (p. 28) and an appropriate amount of the acidified extract was used. The portion was evaporated to dryness and extracted with 10 ml. of iso-amyl alcohol. The residue was carefully evaporated to remove the last traces of alcohol, redissolved in water and barium sulphate precipitated. The barium sulphate was filtered off and the subsequent conversion to perchlorates and extraction were exactly as before. The results are shown in Table XI.

TABLE XI.

Silicate Used	Percentage of Potash.	
	Bureau of Standards	Experimental
FELDSPAR	12·58	12·38, 12·59 } 12·49
PLASTIC CLAY	3·20	3·26, 3·24, 3·25, 3·35 } 3·27
BURNT REFRACTORY	1·37	1·51, 1·55 } 1·53
INCHCOLM PICRITE	0·49	0·41, 0·56 } 0·49

Again the figures for the 'Burnt Refractory' are considerably higher than that given by the Bureau

of Standards. The other results are in reasonable agreement with those of previous analyses.

This method had one of the disadvantages of Method (a), namely, there was often considerable delay in the preliminary removal of calcium chloride, owing to the clogging of the fine glass pores of the immersion filter by the finely divided residue, suspended in the almost syrupy solution of calcium chloride in iso-amyl alcohol. Mainly because of this it was decided to examine the method involving the precipitation of potassium as potassium sodium cobaltinitrite, followed by its separation and weighing as potassium perchlorate. The precipitation as cobaltinitrite would eliminate the sulphate,[10] and at any rate, the bulk of the calcium salts.

Method (c). The Determination of Potassium as Potassium Perchlorate after prior Precipitation as Potassium Sodium Cobaltinitrite.

As stated in the introduction, it was not intended, owing to the variable composition of the cobaltinitrite precipitate, to determine potassium as potassium sodium cobaltinitrite . Instead, it was proposed to convert the cobaltinitrite precipitate to the mixed perchlorates.[14] In determining potassium as potassium perchlorate, after precipitation as

potassium sodium cobaltinitrite, the most important factor is to ensure the initial quantitative separation of the potassium.

The most recent work on the subject[12] advocates the use of two separate potassium-free reagents, namely, solutions of sodium nitrite and cobalt nitrate, in presence of a saturated sodium chloride solution. This method was first of all adopted.

A mixture of potassium chloride (0·1 gm. or 0·005 gm.), 0·1 gm. of sodium chloride, and 1·2 gm. of hydrated calcium chloride, in three or four ml. of water, made just acid with hydrochloric acid, was evaporated to dryness in a 250 ml. beaker (this large size of beaker was necessary owing to the effervescence during the conversion of the cobaltinitrite precipitate to perchlorate). The residue was allowed to cool and 1·5 ml. of glacial acetic acid and 10 ml. of a saturated aqueous sodium chloride solution were added in succession. After 5 to 10 minutes, 5 ml. of a 30% aqueous solution of sodium nitrite were added, and the contents of the basin stirred until all soluble substances were dissolved. After a further 5 to 10 minutes (but not longer) 5 ml. of a 20% aqueous solution of cobalt nitrate were added rapidly, with constant stirring. Instead of leaving the beaker overnight, as recommended by Piper, the liquid, after 30 minutes' mechanical stirring, was removed by means of the small immersion filter (p. 9). The precipitate was washed

with ten 1-ml. portions of the wash-liquid used by Piper, namely, a filtered saturated solution of the potassium cobaltinitrite precipitate in water, each portion being drawn away before addition of the next. The requisite amount of perchloric acid, according to the amount of precipitate, was added, with the immersion filter still present, and the beaker was covered with a split clock-glass. Gentle warming dissolved the precipitate, the operation being carried out very carefully, as there was considerable effervescence and risk of loss by spurting, and, after cooling somewhat, the filter was thoroughly rinsed, inside and out, with boiling water. The solution was transferred to the weighed platinum basin and the subsequent removal of perchloric acid and the two extractions with the ethyl acetate - n-butyl alcohol mixture were carried out exactly as in the previous methods, the potassium perchlorate being finally dried and weighed.

A correction of -0·0010 gm. (potassium chloride) had to be applied for potassium in the reagents, and the final results were low by about 2% on the larger amount of potassium chloride and by 15% to 20% on the smaller. No doubt omitting to leave the cobaltinitrite precipitate to settle overnight before filtration was responsible for the negative errors. As it was desired to determine potassium more expeditiously than Piper's method will allow, no further experiments were made.

The second method adopted for precipitating the potassium consisted in evaporating the same constituents as before with a sodium cobaltinitrite reagent prepared exactly according to Hamid's instructions[10]. The reagent was filtered through a sintered Jena glass crucible (No. 10 G4) immediately before use, and was never kept longer than one month.

10 ml. of the reagent were added to the same mixture of salts as was used in methods (a) and (b), and the whole was evaporated to dryness in a 250 ml. beaker. The perfectly dry mass was stirred up with 10 ml. of 5% acetic acid and the liquid removed with the immersion filter. The residue was then washed with five 1-ml. portions of the saturated potassium sodium cobaltinitrite wash-liquid and converted to the perchlorates as before.

This method required no correction for potassium in the reagents, and was accordingly adopted for subsequent work. The table given below shows the results for varying amounts of potassium chloride.

TABLE XII.

KCl Used (gm. × 10^4)	KCl Found (gm. × 10^4)	Error (gm. × 10^4)
1000	1001	+1
	999	-1
500	496	-4
	498	-2
50	50	0
	49	-1

The Determination of Potash in Silicates by Method (c).

Potash was determined in the silicates 'Feldspar, No. 70', 'Opal Glass, No. 91', 'Plastic Clay, No. 98', and 'Burnt Refractory, No. 76' of the American Bureau of Standards, and in 'Inchcolm Picrite' analysed by T.C.Day.[23] 0·5 gm. of the silicate was decomposed as before by the method of Lawrence Smith, and the requisite amount of the slightly acidified extract was evaporated to dryness with 10 ml. of the cobaltinitrite reagent, and extracted with 10 ml. of 5% acetic acid. The residue was washed with the saturated potassium sodium cobaltinitrite wash-liquid and converted to the perchlorates. These were extracted twice with the ethyl acetate - n-butyl alcohol mixture, and the residual potassium perchlorate dried and weighed. The results are shown in Table XIII.

TABLE XIII.

Silicate Used	Percentage of Potash	
	Bureau of Standards	Experimental
FELDSPAR	12·58	12·60, 12·69, 12·57 } 12·62
PLASTIC CLAY	3·20	3·25, 3·23 } 3·24
OPAL GLASS	3·24	3·34, 3·39 } 3·37
BURNT REFRACTORY	1·37	1·61, 1·60 } 1·61
INCHCOLM PICRITE.	T.C. Day's figure: 0·49	0·42, 0·41 } 0·42

Finally, Table XIV gives a summary of the figures obtained in determining potash in silicates by the three methods previously outlined (pp. 40, 43, 49).

TABLE XIV.

Silicate Used.	Percentage of Potash in Silicate.							Maximum Deviation allowed by Washington.
	Bureau of Standards.	Experimental, Method (a).	Maximum Deviation from Mean, Method (a).	Experimental, Method (b).	Maximum Deviation from Mean, Method (b).	Experimental, Method (c).	Maximum Deviation from Mean, Method (c).	
FELDSPAR	12·58	12·56		12·38 12·59 } 12·49	±0·1	12·60 12·69 12·57 } 12·62	±0·06	±0·1
PLASTIC CLAY	3·20	3·12 3·30 } 3·21	±0·09	3·26 3·24 3·25 3·35 } 3·27	+0·08 -0·03	3·25 3·23 } 3·24	±0·01	±0·05
OPAL GLASS	3·24					3·34 3·39 } 3·37	±0·03	±0·05
BURNT REFRACTORY	1·37	1·60 1·65 } 1·63	±0·03	1·51 1·55 } 1·53	±0·02	1·61 1·60 } 1·61	±0·01	±0·05
Inchcolm PICRITE.	T.C. Day's figure. 0·49			0·41 0·56 } 0·49	±0·07	0·41 0·42 } 0·42	±0·01	±0·03

It is noteworthy that in method (c) alone do the maximum deviations from the mean lie consistently within the limits allowed by Washington. From the practical point of view method (c) was preferred to method (b), because of its somewhat greater speed and simpler technique. Method (a), although yielding results similar to those given by the other two methods, is not recommended for the reasons previously stated (p. 41).

The mean percentages obtained by all three methods are in fair agreement with the certificate values. It will be observed that the general tendency to slightly high figures for potash, as compared with the certificate values, is balanced by the slightly low figures obtained throughout for soda (Table V). The certificate values are based on the use of standard procedures, involving the weighing of the alkali chlorides. It is difficult at present to indicate the significance of the above observations.

LITHIUM.

Very little work has been done on the subject of finding new reagents for the determination of lithium. As Barber and Kolthoff[5] found that their zinc uranyl acetate reagent for sodium was sensitive to more than 0·2 mg. of lithium chloride per ml., it was thought that it might be profitable to examine more closely the formation of, presumably, triple acetates of lithium, under conditions analogous to those for sodium.

The Preparation of Triple Acetates of Lithium.

While investigating the magnesium uranyl acetate reagent for sodium, Blanchetière[24] prepared complex uranyl acetates containing, in addition to sodium, copper, zinc, cadmium, thorium, calcium, barium, manganese, mercury and lead, in an attempt to find one more insoluble than the magnesium salt. Similar experiments were made here. Solutions containing uranyl acetate and another acetate were prepared in a manner similar to the zinc uranyl acetate reagent used for sodium, zinc acetate being replaced by the same weight of the other acetates. The acetates employed were those of zinc, barium, cadmium, calcium, copper, lead, manganese, magnesium, mercury, nickel and cobalt. Qualitative tests were made by adding 10 ml. of the reagent to 1 ml. of a 1% solution of lithium chloride in water. The zinc and nickel uranyl acetates, although

giving a copious precipitate with sodium, were selected as giving the largest and most immediate precipitate with lithium.

The relative solubilities of sodium zinc uranyl acetate, lithium zinc uranyl acetate and lithium nickel uranyl acetate were tested approximately by adding water, drop by drop, from a micro-burette, to 0·1 gm. of each solid, shaking after the addition of each drop. Sodium zinc uranyl acetate required 1·84 ml. for complete solution, while the lithium salts required 1·41 and 1·44 ml. respectively. The solubilities of the lithium triple salts were thus similar and not much greater than that of sodium zinc uranyl acetate.

Preliminary quantitative experiments were made with the two reagents cited above. A 1% neutral solution of lithium chloride was prepared by dissolving approximately 2·2 gm. of lithium carbonate in hydrochloric acid in a platinum basin, evaporating to dryness, dissolving in water, diluting to 250 ml. and weighing in a stoppered flask. To 1 gm. of this solution (which thus corresponded to 0·01 gm. of lithium chloride) in a 50 ml. beaker, were added 10 ml. of the filtered reagent. The mixture was mechanically stirred for 15 minutes and set aside for 15 minutes. At the end of this time the solution was filtered through a weighed Jena sintered glass crucible (No. 10 G3), the disc of which was covered with a thin layer of asbestos, washed with five 2-ml. portions of the reagent and with five 2-ml portions

of a filtered saturated solution of the corresponding triple salt in 95% alcohol. The alcohol was then removed with three 2-ml. portions of redistilled ether, and the crucible and contents were finally heated at 40°, cooled and weighed. All determinations were carried out in a thermostat near room temperature. Assuming the triple salts to be analogous to that of sodium, viz. $LiNi(UO_2)_3(CH_3COO)_9.6H_2O$ and $LiZn(UO_2)_3(CH_3COO)_9.6H_2O$ the weights of the precipitates corresponded to a recovery of only 40% to 60% of lithium, the yields of the nickel salt being superior to those of the zinc salt. Saturating the reagents with the appropriate lithium triple acetate and increasing the amount of the precipitants did not materially improve the results. Experiments carried out with reagents diluted with an equal volume of absolute alcohol and filtered before use were similarly ineffective in increasing the percentage recovery. The poor recoveries were not due to solubility losses, as 30-ml. portions of ether, of the alcoholic wash-liquid and of the precipitating reagent had comparatively small solvent effects on the precipitates.

The Partial Analysis of Lithium Nickel Uranyl Acetate.

As the nickel uranyl acetate reagent had given the better results, a few partial analyses of the precipitate were made, to find if a compound of the composition $LiNi(UO_2)_3(CH_3COO)_9.6H_2O$ was indeed being

formed. Nickel and uranium were determined in the following manner.

Nickel in the triple salt was precipitated with dimethylglyoxime, the procedure being modified for the presence of uranium. For preliminary experiments, 10 ml. of a solution of nickel acetate containing approximately 0·06 gm. of nickel were used. To this 3 ml. of dilute hydrochloric acid and 10 gm. of tartaric acid were added, the solution was diluted to about 300 ml. and heated to 80°, and 40 ml. of a 1% solution of dimethylglyoxime in alcohol were run in. The solution was made slightly alkaline with ammonia and, after boiling for a few minutes and cooling, the scarlet precipitate was filtered through a Gooch crucible and washed with cold water.[25] The crucible was dried at 120°. Almost identical results were obtained with nickel alone and in presence of uranyl acetate equivalent to that which would be present in the triple salt.

0·2 gm. of the triple salt was dissolved in hot dilute hydrochloric acid, tartaric acid was added and the nickel was precipitated as before.

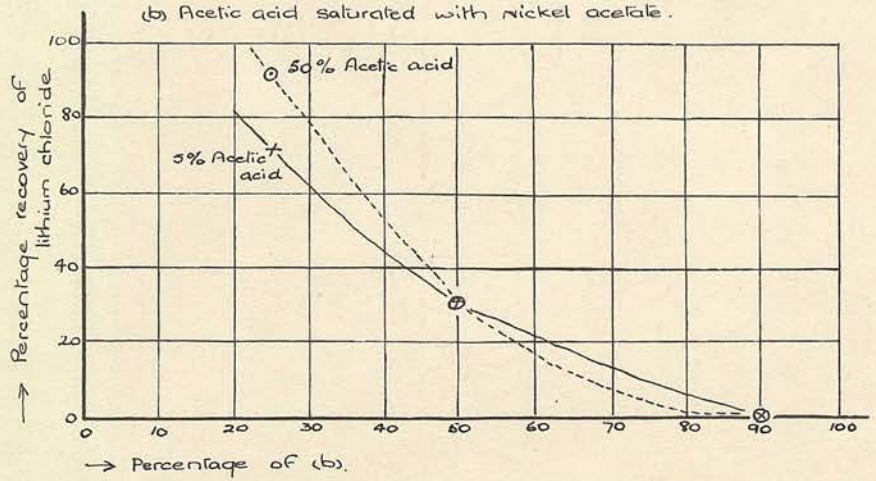
Uranium in the triple salt was determined by the method of Kolthoff and Lingane[26] which consisted of reducing the uranium to a mixture of U^{III} and U^{IV}, oxidising to U^{IV} with air, and oxidising to U^{VI} with potassium dichromate, using ferric ion as catalyst. The reducing agent was a zinc reductor, through which 50 ml. of 5% sulphuric acid had been passed. The

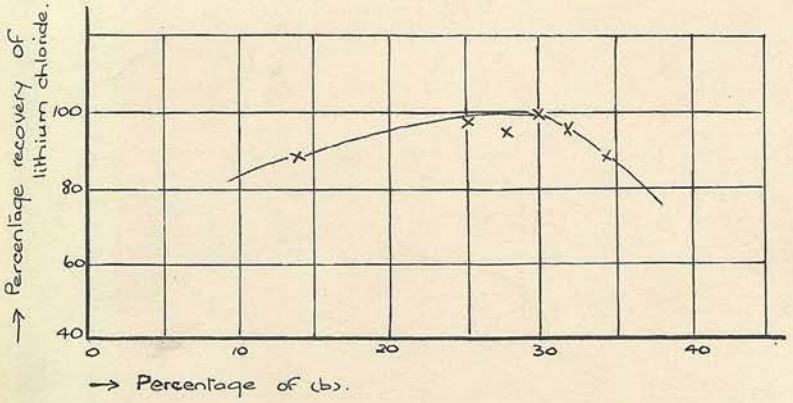
uranium solution was diluted to 100 ml., 5 ml. of concentrated sulphuric acid were added, and the mixture was cooled and passed through the reductor with gentle suction. (50 ml. per minute). The reductor was rinsed with three 30-ml. portions of 5% sulphuric acid, followed by three 35-ml. portions of distilled water. Washed air was bubbled through the solution for 5 to 10 minutes to oxidise the U^{III} to U^{IV}. To the solution were added 25 ml. of a 2% ferric chloride solution, 15 ml. of 85% phosphoric acid and ten to twelve drops of a 0·2% solution of barium diphenylamine sulphonate as indicator. The whole was titrated slowly with 0·1 N potassium dichromate solution until one drop of the latter produced a strong violet colour, persisting for over one minute. Nickel was found to have no effect when added, as nickel acetate, to 20 ml. of a uranyl acetate solution containing approximately 0·1 gm. of uranium, in an amount equivalent to that which would be present in the triple salt. 0·2 gm. of the triple salt was dissolved in 10 ml. of dilute sulphuric acid, diluted and treated as above.

The nickel and uranium contents of the triple salt were found to be 3·77% and 47·7% respectively, as against the theoretical figures of 3·87 and 47·2 required for a precipitate of the composition $LiNi(UO_2)_3(CH_3COO)_9.6H_2O$. These results indicate that the triple salt of this composition was being precipitated, and that the low yield was due to incomplete precipitation.

GRAPH A.

(a) Acetic acid saturated with uranyl acetate.
(b) Acetic acid saturated with nickel acetate.

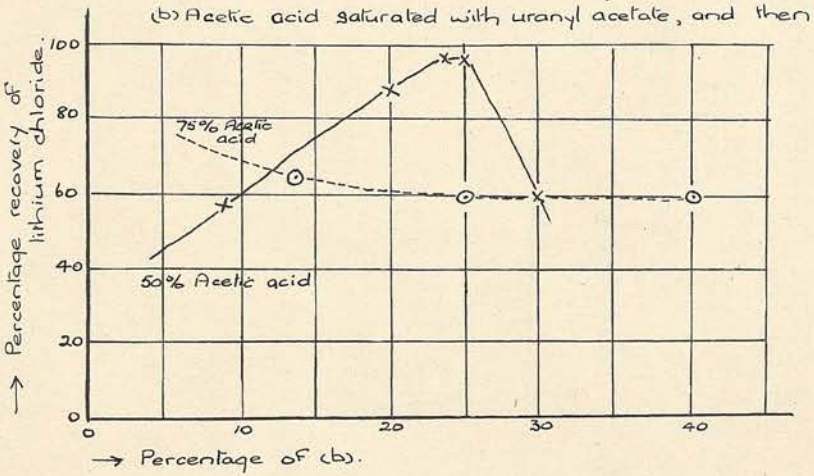


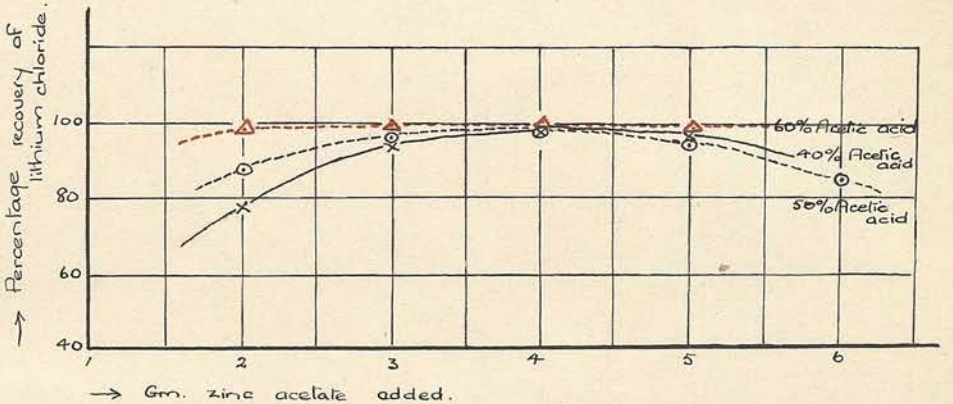


(a) 50% Acetic acid saturated with uranyl acetate
(b) 50% Acetic acid saturated with uranyl acetate, and then with zinc acetate.

GRAPH B.

(a) Acetic acid saturated with uranyl acetate
(b) Acetic acid saturated with uranyl acetate, and then with nickel acetate.





Zinc acetate added to 40 ml. of acetic acid; the solution saturated with uranyl acetate.

58(a).

The Quantitative Precipitation of Lithium.

It was sought to improve the yield of triple salt by experimenting with double acetate reagents containing varying amounts of nickel and uranium acetates and of acetic acid.

Graph A shows the results of the first experiments in which precipitating reagents were prepared by mixing different volumes of saturated solutions of nickel acetate and of uranyl acetate in 5% acetic acid, and similar solutions in 50% acetic acid. The curves show quite clearly that the percentage recovery of lithium increases with increasing uranyl acetate content of the reagent, and also with increasing concentration of acid.

In the experiments recorded on Graph B, the two solutions to be mixed consisted of (a) acetic acid ~~and~~ saturated with uranyl acetate, and (b) acetic acid saturated first with uranyl acetate and then with nickel acetate, the object being to increase the proportion of uranyl acetate in the final reagent. Different volumes of (a) and (b) were mixed, and the graph shows the results for reagents prepared from 50% acetic acid and from 75% acetic acid. The 75% acetic acid reagents did not give more than 70% recovery, while with the 50% acetic acid reagents the percentage recovery of lithium rose sharply to a maximum when 25% of (b) was present.

As the highest yield obtained, even when the reagents were saturated with the triple salt, was,

however, only 95% of the theoretical $[LiNi(UO_2)_3(CH_3COO)_9.6H_2O]$ it was decided to experiment further with the zinc uranyl acetate reagent.

Two solutions were prepared as before, (a) 50% acetic acid saturated with uranyl acetate, and (b) the same acid saturated with uranyl acetate and then with zinc acetate. When different volumes of (a) and (b) were mixed, the reagents obtained gave the results indicated in Graph C. The percentage recovery rose fairly sharply to about 100% for reagents containing between 25% and 30% of (b).

Finally, as it was quite obvious that the maximum amount of uranyl acetate was required, reagents were made up by adding varying weights of solid zinc acetate to 40 ml. of 40%, 50% and 60% acetic acid and saturating the solutions with uranyl acetate at the thermostat temperature. Lithium zinc uranyl acetate was added, in excess, to the reagents, which were kept in the thermostat overnight in stoppered bottles. The next morning they were mechanically stirred and filtered before use. The results of determinations made with each reagent (according to the method on p. 54) are shown in the following table and on Graph D. The latter shows the weight of zinc acetate plotted against the percentage recovery of lithium chloride for the three acid concentrations.

TABLE XVI.

Wt. of LiCl Used = 0·01000 gm.

Wt. of Zinc Acetate in 40 ml. $Zn(CH_3COO)_2 3H_2O$ (gm.)	Percentage Recovery of Lithium Chloride		
	40% Acetic Acid	50% Acetic Acid	60% Acetic Acid
2	75·7	87·8	98·1
3	94·0	97·2	100·1
4	99·6	98·1	98·8
5	95·8	96·4	99·7
6		95·1	

From these results it is evident that 60% acetic acid gives the best reagent and that, allowing an experimental error of about 1%, which is by no means excessive, theoretical results are obtained over a range of 3 to 5 gm. of zinc acetate. The reagent selected for all further determinations contained 5 gm. of zinc acetate per 40 ml. of 60% acetic acid and was saturated with uranyl acetate and then with the triple acetate. It was found in practice that the reagent deteriorated on standing, owing to the instability of uranium solutions in the light, and that the yields of triple acetate diminished by as much as 10% in three weeks. This was counteracted by keeping it in a dark glass bottle and making it up fresh every month.

The Characteristics of Lithium Zinc Uranyl Acetate.

Lithium zinc uranyl acetate precipitated by this reagent differed considerably in appearance from the corresponding sodium salt, being rather more green in colour, more finely divided and much less crystalline in appearance. As previously indicated (p. 54), it was somewhat more soluble in water than the sodium salt. The respective solubilities of the precipitate in absolute and 95% aqueous ethyl alcohol were found to be 0·2236 gm. and 0·1934 gm. per 100 ml. of solvent. The 95% alcoholic wash-liquid, saturated with the triple salt, was therefore retained in future experiments.

The Analysis of Lithium Zinc Uranyl Acetate.

Precipitates from a freshly prepared reagent were analysed for zinc, uranium and water, and others were converted by treatment with sulphuric acid to the mixed sulphates.

Zinc in the triple salt was determined by precipitation with 8-hydroxyquinoline, the customary method being modified for the presence of uranium.[27] For preliminary experiments a standard zinc sulphate solution was made up containing about 3·7 gm. of hydrated zinc sulphate in 250 ml., and 10 ml. portions were used, with 0·65 gm. of uranyl acetate added. 100 ml. of an alkaline malate solution (82 gm. of malic acid, 49·5 gm. of caustic soda per litre) were added to

the neutral zinc-uranium solution, thus converting the uranium to the soluble malate and preventing its co-precipitation with zinc. The solution was warmed to 60°, the reagent added slowly to excess (shown by a dark green colour) and the mixture filtered cold through a 7-cm. "white band" paper. As the precipitate was a dark green colour, instead of the usual canary yellow, it was considered advisable to dissolve it in dilute hydrochloric acid and reprecipitate it with a few drops of the reagent and sodium hydroxide in excess; the reprecipitated zinc complex was much more normal in colour. The solution was filtered through a weighed sintered Jena glass crucible (No. 10 G4) heated at 120° and weighed as the anhydrous complex. The results were 0·8% high. Approximately 0·7 gm. of lithium zinc uranyl acetate was then dissolved in about 15 ml. of hot water, alkaline malate solution was added, and the zinc precipitated twice in the same manner. The requisite correction was applied to the result for the triple salt.

Analysis of the triple salt for uranium was carried out by the method of Kolthoff and Lingane,[26] exactly as for the lithium nickel uranyl acetate (p.56).

Analysis of the triple salt for water presented considerable difficulty as the water was very tenaciously held. Barber and Kolthoff[5], in their determinations of water in the sodium triple salt recommend heating at 90° under 30 mm. pressure, but give no experimental

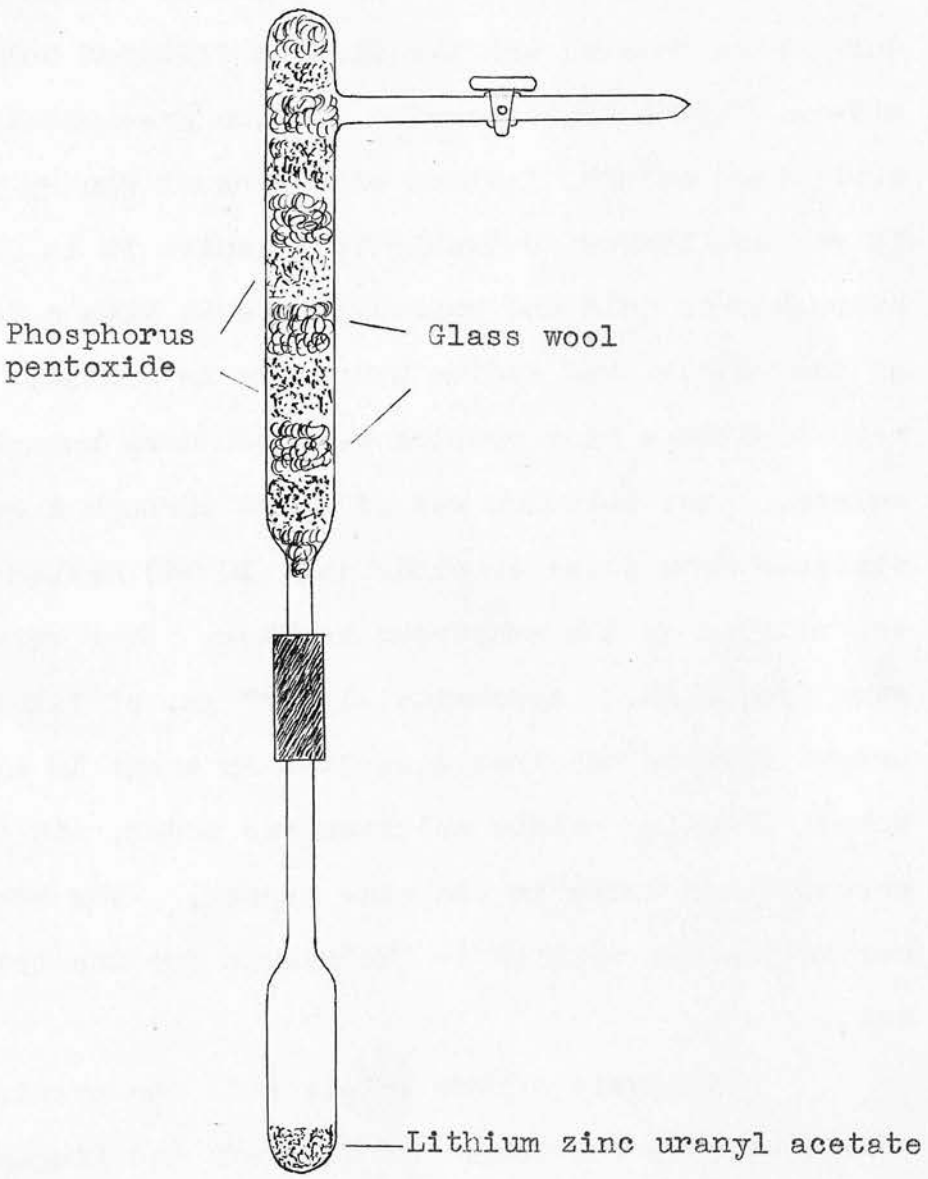

Phosphorus
pentoxide
Glass wool
Lithium zinc uranyl acetate

Fig. II.

details. Various types of apparatus were tried, but the most satisfactory form was found to be that shown in Fig. II. The bulb, containing a weighed amount of triple salt, was connected by heavy pressure tubing to a 1-inch wide tube containing layers of phosphorus pentoxide and glass wool. The tube and bulb were evacuated, as far as possible, through the side-tube, the end of which was drawn off in the Bunsen flame. All connections were sealed over with wax, and the bulb was inserted in a hole at the top of an oven, regulated to about 100°, and insulated by means of sheets of asbestos. At the end of a week, in two experiments, and a fortnight, in a third, the apparatus was cooled, air was allowed to enter (through the pentoxide) and the bulb was re-weighed. The dehydrated triple salt slowly regained weight on being exposed to moist air and the original weights (±1mg.) were eventually reached. This showed that there was no decomposition of the triple salt beyond removal of water.

For the conversion to the mixed sulphates, two 0·7 gm. portions of triple salt in platinum crucibles were dissolved in 10 ml. of dilute sulphuric acid and heated gently in air-baths, until all sulphuric acid was expelled. The residues were redissolved in a little water and evaporated again. The crucibles were then heated to constant weight at 500° in an electric furnace.

The following table shows the results of the analyses, together with the theoretical values required by precipitates of the compositions $LiZn(UO_2)_3(CH_3COO)_9.6H_2O$ and $LiZn(UO_2)_3(CH_3COO)_9.7H_2O$.

TABLE XVII.

	Percentage of Zinc	Percentage of Uranium	Percentage of Water	Wt. of Mixed Sulphates (gm.)	
				1	2
Calculated as $LiZn(UO_2)_3(CH_3COO)_9.7H_2O$	4·24	46·41	8·18	0·5700	0·5446
Calculated as $LiZn(UO_2)_3(CH_3COO)_9.6H_2O$	4·30	46·96	7·10	0·5768	0·5510
Experimental	4·37 4·38	47·55 47·00 47·66 47·06	7·70* 7·91* 8·14ø	0·5758	0·5510

* Dehydration for one week

ø " " two weeks.

The results favour, on the whole, the composition $LiZn(UO_2)_3(CH_3COO)_9.6H_2O$. At present it is not clear why the percentage of water found contradicts the results of the other determinations. In the following work the hexahydrate composition has been assumed throughout.

The Quantitative Precipitation of Varying Amounts of Lithium Chloride.

Precipitations of amounts of lithium chloride varying from 0·01 gm. to 0·0006 gm. were now carried through according to the method on p. 54 . It was found that while the large amount of lithium chloride gave satisfactory results when precipitated from 1 ml. of solution, it was necessary to precipitate the smaller quantities after evaporation until solid separated.

The completeness of precipitation of lithium chloride was investigated by precipitating twice, as in the method for sodium. The first precipitate was dissolved in not more than 10 ml. of 0·1 N hydrochloric acid, the solution was evaporated down and the lithium reprecipitated with 10 ml. of the reagent. As in the single precipitation, the large amounts were precipitated from 1 ml., while the smaller amounts were precipitated after evaporation until solid just appeared.

In later experiments where the first precipitate was not weighed, a procedure similar to that adopted in the case of sodium was used. The first precipitate was washed with the reagent as usual and then with two 1-ml. portions of the alcoholic wash-liquid, the suction being removed during the washing. The precipitate was then dissolved in 10 ml. of 0·1 N hydrochloric acid, the solution evaporated and precipitation effected as usual.

The following table shows the results for single and double precipitations of the lithium triple acetate.

TABLE XVIII.

LiCl Used (gm. x 10^5)	LiCl Found (one pptn.) (gm. x 10^5)	LiCl Found (two pptns.) (gm. x 10^5)	Error after one pptn. (gm. x 10^5)	Error after two pptns. (gm. x 10^5)
1000	995		-5	
	997		-3	
	997		-3	
	999		-1	
300	297		-3	
200	201		+1	
60	60		0	
	60		0	
1000	997	997	-3	-3
		1006		+6
200	196	196	-4	-4
		201		+1
60		57		-3
		61		+1

The results based on one precipitation may be regarded as satisfactory, in view of the high solubility of the precipitate in aqueous solutions. Those referring to two precipitations are more irregular. The evaporation process preceding the second precipitation required a good deal of careful observation.

An important fact emerges from the above results, namely, that the yield of precipitate after

two precipitation processes is not appreciably different from that obtained after one. This indicates that the precipitation of the lithium is quantitative.

The Precipitation of Lithium Zinc Uranyl Acetate in Presence of Various Salts.

Since the precipitation of lithium as lithium zinc uranyl acetate was to be applied to the determination of lithium in the aqueous extract obtained after decomposing a silicate by the Lawrence Smith method, the effect of the addition of the various salts which would be present in the silicate extract was examined.

Addition of the reagent to separate solutions containing potassium chloride, calcium chloride and sodium chloride was made; no precipitate was formed with the first two, but there was a copious precipitate with sodium chloride.

As sodium chloride and consequently, probably potassium chloride would have to be separated from lithium chloride, prior to precipitation of the lithium triple salt, the effect of small amounts of these salts was now investigated, to find out whether their removal would have to be absolutely quantitative. The addition of 0·003 gm. of potassium chloride had only a small effect on the precipitation of 0·01 gm. of lithium chloride, but 0·0005 gm. of sodium chloride added to the same amount of lithium chloride gave a large positive

error, actually greater than anticipated from the amount of sodium chloride added. As double precipitation of the sodium-contaminated lithium triple acetate would be useless, quantitative separation of the sodium and lithium chlorides would be necessary.

The influence of calcium was next investigated. 1·2 gm. of hydrated calcium chloride (i.e. the amount which would be present in the total silicate extract) were added to 0·01 gm. of lithium chloride, and the lithium triple acetate precipitated from 1 ml. with 10 ml. of reagent. There was only 80% recovery; this showed that lithium could not be determined, without modification of the prescribed method, in the total extract. Quantities corresponding to one-tenth of the extract were tried, 0·12 gm. of calcium chloride being added to amounts of lithium chloride varying from 0·01 gm. to 0·0006 gm. The results were high, but figures nearer the theoretical were obtained by dissolving the precipitates and reprecipitating them as described on p. 65. The results, which are shown in Table XIX are rather irregular, but comparable with those shown in the preceding table.

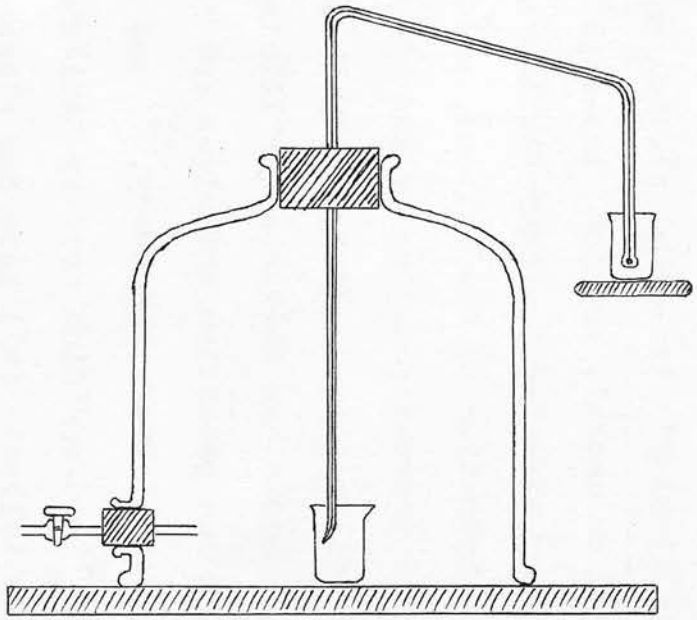
TABLE XIX.

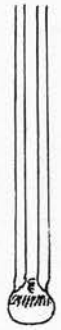
Wt. Added Salt (gm.)	LiCl Used (gm. × 10^5)	LiCl Found one pptn. (gm. × 10^5)	LiCl Found two pptns. (gm. × 10^5)	Error after one pptn. (gm. × 10^5)	Error after two pptns. (gm. × 10^5)
KCl : 0·003	1000	1005		+5	
NaCl : 0·0005	1000	1059		+59	
$CaCl_2.6H_2O$: 1·2	1000	789		-211	
$CaCl_2.6H_2O$: 0·12	1000	1034		+34	
" "		1028	1001	+28	+1
" "	200		207		+7
" "			194		-6
" "	60		55		-5
" "			56		-4

The Separation of Lithium Chloride from Sodium Chloride in Mixtures containing Calcium, Potassium and Sodium Chlorides.

Owing to the precipitation of both sodium and lithium chlorides by the lithium reagent, quantitative separation of lithium chloride, with or without calcium chloride, from the amount of sodium chloride which would be present in the extract after fusion of a silicate by the Lawrence Smith method, had to be considered. For this purpose, it was thought that extraction of lithium chloride with an organic solvent would be most useful, and in particular, the method of Moser and Schutt[28] was studied. These workers set out to improve Winkler's iso-butyl alcohol method,[29] which was based on Gooch's original iso-amyl alcohol method.[30] They effected considerable improvement by more careful dehydration of the solvent, and by use of a siphon tube to prevent creeping of the alcoholic solvent during filtration. In this way they obtained good results. Three other solvents for lithium chloride, in which sodium and potassium chlorides are insoluble, are acetone, used by Brown and Reedy,[31] ~~and~~ dioxan, used by Sinka,[32] and pyridine used by Kahlenberg & Krauskopf.[33]

These solvents fall into two classes, those which dissolve calcium chloride along with the lithium chloride (in particular, the alcohols) and those which dissolve, at most, only a very small amount of calcium chloride (acetone, pyridine, and dioxan). The former





Immersion capillary filter,
actual size.

Fig. III.

would involve a double precipitation of lithium zinc uranyl acetate, the latter only one precipitation.

In the present work, synthetic mixtures were prepared containing the amounts of the mixed salts that might be present in one-tenth of the extract obtained by decomposing half a gram of silicate by the Lawrence Smith method. Amounts of lithium chloride varying from 0·01 gm. to 0·0006 gm. were used. These limits represent 9% and 0·6% of lithia in a silicate.

Owing to the creeping tendency of organic solvents, it was found to be impossible to filter the extracts directly, and use was made of a capillary immersion filter, by means of which the extract, contained in a 30-ml. beaker, was passed into another beaker within a Gibson filtration apparatus (Hillebrand and Lundell, p. 92). The filter was made by widening out 1 mm. internal diameter capillary tubing to a small bell-shaped end. A tiny spiral of very fine platinum wire was inserted, to prevent blocking of the capillary, and a little asbestos suspended in water was drawn up.[34] The capillary tubing was bent at the angles shown in Fig. III, and the other end was drawn off to a slanting point, which rested against the receiving beaker. Suction was adjusted to draw the liquid over gradually, and when as much as possible had been removed, the beaker containing the residue was lowered a few inches and the contents washed round with not more than 1 ml. of the solvent. The beaker was raised again and the

solvent drawn through the filter. When the washing had been repeated the requisite number of times, the beaker containing the residue was replaced by a clean beaker. After rinsing any residual solvent in the filter tube over into the beaker containing the residue, with 1 ml. of absolute ethyl alcohol, the filter was washed by drawing through three 1-ml. portions of boiling water into the same beaker. This was again followed by 1 ml. of absolute ethyl alcohol and finally by 1 ml. of the requisite solvent, leaving the filter ready for the next extraction.

Preliminary experiments were carried out with iso-amyl alcohol, acetone, pyridine and dioxan as solvents. The last two solvents were not investigated in detail as they were found to be quite unsuitable. Pyridine, apart from its objectionable odour, even when all work was carried out in a well-ventilated fume-cupboard, gave solutions that were very difficult to filter, and the results obtained were low. Dioxan solutions were not only slow-filtering, but the solvent formed a considerable amount of resinous matter, from which no lithium triple salt could be precipitated. The solvent had not, however, been specially purified.

For the iso-amyl alcohol extractions, mixtures containing lithium chloride (0·01 gm. to 0·0006 gm.), potassium chloride (0·01 gm.), and calcium chloride (0·12 gm.), and mixtures containing the same constituents with the addition of sodium chloride (0·01 gm.), were

used. The mixed salts, in a 30 ml. beaker, were evaporated to dryness on the electric boiler and re-evaporated with 1 ml. of iso-amyl alcohol, to ensure complete dehydration. 10 ml. of iso-amyl alcohol (later 5 ml. were used) were then added, and the mixture was heated almost to boiling, with the addition of a small drop of concentrated hydrochloric acid (to convert to lithium chloride any lithium hydroxide formed). The hard mass was thoroughly broken up with a glass rod and allowed to cool. The alcoholic solution was removed by means of the filtration apparatus, described above, and the residue was washed with five 1-ml. portions of the solvent. As the residue with this solvent is very finely divided and tends to clog the asbestos, the filter was plugged with a paper disc, cut from an ashless filtration accelerator. The residue was dissolved in water, re-evaporated, extracted with five ml. of the solvent and washed five times. The extract and washings were collected in the same beaker as before, evaporated, dissolved in hot water and re-evaporated to dryness. As the bulk of the calcium chloride was dissolved by the iso-amyl alcohol, a double precipitation of lithium zinc uranyl acetate was necessary, the procedure being in accordance with the amount of lithium present (p. 65). The results appear in Table XX.

With the volumes of iso-amyl alcohol mentioned above, the results for lithium show a definite high tendency, rather more marked in presence of sodium

chloride, which is slightly soluble in iso-amyl alcohol. By direct experiment, 100 ml. of the solvent were found to dissolve 1·4 mg. of sodium chloride at room temperature. In order to diminish solubility errors, the volumes of iso-amyl alcohol were cut down to 2 ml. for the first extraction with three ½-ml. washes, followed by 1-ml. for the second extraction and five ½-ml. washes. As the results in the table show, there was no proportionate decrease in the positive error, nor was any improvement noted by reducing the amounts of sodium and potassium chlorides to 0·005 gm of each. The results on the whole are rather poor and irregular, and it was thought that a method involving one precipitation of zinc uranyl acetate would be preferable.

TABLE XX.

Volumes of Alcohol used for Extraction (ml.)	Volumes of Alcohol used for Washing (ml.)	LiCl Used (gm. x 10^5)	LiCl Found (gm. x 10^5)	Error (gm. x 10^5)	Salts present in Addition to $CaCl_2.6H_2O$ (gm.)
10, 5	5, 5	1000	1030	+30	KCl : 0·01
5, 5	5, 5	1000	1009	+9	" "
" "	" "	60	62	+2	" "
2, 1	1·5, 2·5	1000	1010	+10	KCl : 0·02
" "	" "		1013	+13	" "
" "	" "	200	208	+8	" "
" "	" "		205	+5	" "
" "	" "	60	58	-2	" "
" "	" "		58	-2	" "
10, 5	5, 5	1000	1035	+35	KCl : 0·01 NaCl: 0·01
5, 5	5, 5	1000	1015	+15	" "
" "	" "	60	71	+11	" "
2, 1	1·5, 2·5	1000	1007	+7	" "
" "	" "		1003	+3	" "
" "	" "	200	212	+12	" "
" "	" "		213	+13	" "
" "	" "	60	74	+14	" "
" "	" "		65	+5	" "
" "	" "		62	+2	" "
" "	" "	1000	1035	+35	KCl : 0·005
" "	" "		1036	+36	NaCl: 0·005 " "

A mixture of four parts of acetone and one part of iso-amyl alcohol was next used for extraction purposes, but the results showed no improvement on those with iso-amyl alcohol alone. The bulk of the calcium chloride was dissolved, and a double precipitation of lithium zinc uranyl acetate was again necessary.

Experiments with similar amounts of salts were performed in the same way, using, as solvent, acetone, which does not dissolve appreciable amounts of calcium chloride. Here the low boiling-point of acetone was found to be a disadvantage, as it could obviously not be used to dehydrate the mixed salts. Dehydration was consequently effected simply by heating the mixed chlorides at about 150° (over the electric boiler), and the dry salts were allowed to cool in a desiccator containing phosphorus pentoxide. When cool, 5 ml. of acetone and a small drop of concentrated hydrochloric acid were added, and the mixture was gently warmed, not to increase the solubility of the lithium chloride (for lithium chloride is slightly less soluble in warm acetone), but to soften the dry mass, so that it could be broken up more easily. Since the hygroscopic calcium chloride was not dissolved, the mixture was again cooled in the desiccator. Filtration was carried out in the cold. The disc of filter-paper mentioned in connection with the iso-amyl alcohol extractions was removed from the filter, as the acetone solution passed

through much more quickly than the alcoholic solution, and, in addition, it was found that the filter-paper tended to adsorb lithium chloride from the acetone solution. The suction too had to be reduced considerably, as the acetone was easily volatilised at low pressures, with a risk of leaving a little lithium chloride deposited on the filter. 1-ml. portions of acetone were used for washing the residue, the procedure being exactly as above. Re-extractions were carried out in similar fashion.

Lithium in this case was determined in the evaporated extract with only one precipitation as the triple salt, since the amount of calcium chloride dissolved by the acetone was insufficient to cause an appreciable error.

Determinations made with mixtures without sodium chloride, and in presence of sodium chloride, showed mainly negative errors, due presumably to incomplete removal of the lithium chloride. Reduction of the amounts of sodium and potassium chlorides from 0·01 gm. to 0·005 gm. of each did not have much effect, nor did doubling the amounts of acetone used for extraction. Various results are given in Table XXI.

It was found that satisfactory results were only obtainable by increasing the number of extractions to four (three with 5 ml. and three 1-ml. washes, and one with 5 ml. and five 1-ml. washes) for the large amount of lithium chloride (0·01 gm.) and three for the

smaller amounts; i.e., a greater number of extractions with smaller amounts of acetone was more effective than fewer extractions with larger amounts of acetone. The final satisfactory results, in the second half of the table, refer to solutions containing 0·005 gm. each of sodium chloride and of potassium chloride.

The possible effect on the results of sulphate which has not, so far, been considered, was now examined. 0·005 gm. of sodium sulphate was added to the mixed salts, and was found to be without effect (Table XXI).

TABLE XXI.

Volumes of Acetone used for Extraction (ml.)	Volumes of Acetone used for Washing (ml.)	LiCl Used (gm. x 10^5)	LiCl Found (gm. x 10^5)	Error (gm. x 10^5)	Salts present in Addition to $CaCl_2.6H_2O$ (gm.)
5	5	90	94	+4	KCl : 0·01
5, 5, 5	3, 3, 5	1000	966	-34	" "
5, 5	3, 5	60	52	-8	" "
10	5	60	55	-5	KCl : 0·01 NaCl : 0·01
10, 10	5, 5	60	63	+3	KCl : 0·005 NaCl : 0·005
10, 10, 10	5, 5, 5	1000	968	-32	" "
5, 5, 5, 5	3, 3, 3,5	1000	995	-5	KCl : 0·005 NaCl : 0·005
" " " "	" " " "		991	-9	" "
5, 5, 5	3, 3, 5	200	205	+5	" "
" " "	" " "		199*	-1	" "
" " "	" " "	60	57*	-3	" "
" " "	" " "		60*	0	" "
" " "	" " "	50	51	+1	KCl : 0·005 NaCl : 0·005 Na_2SO_4 : 0·005
" " "	" " "		49	-1	" "

Comments on the Method of Determining Lithium.

In the method for the determination of lithium developed here, it might be thought that the four acetone treatments necessary for the quantitative removal of lithium would require more time than would justify the adoption of the method, and that it would be better to employ the usual procedure of removing calcium by precipitation as calcium carbonate. This is not the case, as the extraction process is simpler than the calcium carbonate precipitation, and moreover does not involve adsorption of the lithium chloride by precipitated calcium carbonate, and by filter-paper. As shown below, even if the latter method were used, two acetone treatments would still be necessary to remove 0·01 gm. of lithium chloride from the residual sodium and potassium chlorides (0·005 gm. of each).

TABLE XXII.

No. of Extractions	LiCl Used (gm. x 10^5)	LiCl Found (gm. x 10^5)	Error (gm. x 10^5)	Added Salts (gm.)
1	1000	969	-31	KCl:0·005 NaCl:0·005
1	60	58	-2	" "

The extractions with acetone are very rapid, and the intermediate evaporation and dehydration of the residue can be carried out quite quickly if the wash-water is restricted to those volumes mentioned.

An added advantage is the fact that, if the filter is washed through in the manner recommended, several extractions can be made in succession. For example, if four amounts of lithium chloride are to be extracted, the residue from the first extraction of the first of the set will be ready for a second extraction by the time the last of the set has been extracted for the first time. A series of six determinations has been done in this manner, but four is the most convenient number to handle.

The determination of lithium as lithium zinc uranyl acetate, apart from the extraction process, has this advantage over weighing as sulphate, namely, that a smaller amount of lithium may be determined more accurately, owing to the large weight of the precipitate, compared with its lithium content. The method is also very rapid, a single precipitation being completed (to drying, cooling and weighing the precipitate) within an hour. As with the extractions, a number of precipitations can be done in succession, e.g., consider four determinations, A, B, C and D. Reagent is added to A and the mixture is stirred mechanically in the thermostat for 15 minutes. At the end of this time, reagent is added to B, the stirrer raised from A, rinsed down into A with 2 ml. of reagent and lowered into B which is stirred for 15 minutes, during which time A is set aside in the thermostat. B is then

stopped and set aside, C started and A filtered, washed and dried. This is continued until the four have been completed, intervals between operations being utilised to weigh crucibles.

The Determination of Soda, Potash, and Lithia in Silicates.

It is evident that, where soda and lithia occur together in a silicate, it should be possible to determine them both in the one portion of the silicate extract. As the calcium chloride is left with the sodium chloride in the residue after extraction of the lithium chloride with acetone, it follows that a double precipitation of the sodium as sodium zinc uranyl acetate will be necessary. Another method, however, suggests itself, namely, the removal of the bulk of the calcium chloride by means of the minimum amount of iso-amyl alcohol, followed by the more satisfactory single precipitation of sodium as the triple salt.

Determinations of sodium chloride were made in the residues marked * in Table XXI. In two cases, sodium was precipitated twice as sodium zinc uranyl acetate, according to the standard procedure (p. 26). In a third, the residue, after the removal of lithium chloride, was evaporated to dryness, dehydrated with 1 ml. of iso-amyl alcohol, and 10 ml. of the solvent added. The mixture was heated, and the residue broken up, and the cold solution was filtered, using the capillary immersion filter. No special precautions were taken to remove the last traces of calcium

chloride, and the filter was washed through with boiling water into the beaker containing the residue. The residue was evaporated, dissolved in 1 ml. of water and the sodium triple acetate precipitated with Barber and Kolthoff's reagent.

Both methods required about the same length of time, but the figures below show that the second method gave the better results.

TABLE XXIII.

NaCl Used (gm. x 10^5)	NaCl Found (gm. x 10^5)	Error (gm. x 10^5)	LiCl Used (gm. x 10^5)	LiCl Found (gm. x 10^5)	Error (gm. x 10^5)
(a) Double Precipitation					
500	513	+13	60	57	-3
	513	+13	200	199	-1
(b) Iso-Amyl Alcohol Extraction					
500	497	-3	60	60	0

Since lithia and soda are determinable in one-tenth of the extract obtained after decomposing a silicate by the Lawrence Smith method, and lithium does not interfere with the determination of potassium as the perchlorate, it follows that the methods previously outlined for potassium will apply in presence of lithium, potassium being determined in the major portion of the silicate extract.

Should lithia alone, or lithia and soda only, require to be determined, the customary

procedure could be modified by decomposing 0·05 gm. to 0·1 gm. of the silicate according to Guthrie and Miller's semi-micro-method[6]. In that way the period of decomposition would be considerably reduced, and the total extract would be used for the subsequent determinations.

In conclusion, I wish to express my grateful appreciation to Dr Miller for the interest she has taken in this work, and for the help and encouragement she has given at all times during its progress.

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